United States Patent [19]

Hodgin

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[54]	FORMULA NEMATOI	TION FOR THE CONTROL OF ES						
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[21]	Appl. No.:	775,415						
[22]	Filed:	Sep. 12, 1985						
[51] [52] [58]	U.S. Cl							
[56] References Cited								
U.S. PATENT DOCUMENTS								
		934 Johnson						
	FOREIG	N PATENT DOCUMENTS						
	46-35874 10/1	971 Japan 514/740						

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Primary Examiner—Douglas W. Robinson Attorney, Agent, or Firm—George B. Oujevolk

[57] ABSTRACT

In the control of nematodes, use is made of a formulation using D-limonene as a solvent to carry an effective dosage of chloropicrin. The formulation can also include an amount of methyl isothiocyanate corresponding in volume approximately to the amount of chloropicrin. The combination of these two components is synergistic. With the further addition of diazinon, a double synergistic effect is obtained.

2 Claims, No Drawings

FORMULATION FOR THE CONTROL OF NEMATODES

BACKGROUND OF THE INVENTION

The present invention is directed to the control of undesirable soil components, and more particularly to the control of nematodes, symphylans wireworms, soil borne diseases, and weed seeds in crop land and ornamental gardens as well as commercial turf. Also included in the undesirable components are mole crickets.

nene as a solvent for the chloropicrin. Additionally, methyl isothiocyanate can be included in the formulation. Effective amounts of diazinon, if also added will provide a double synergistic effect, the first synergistic effect being the combination of the chloropicrin and D-limonene and the second synergistic effect will be the addition of diazinon.

SUMMARY OF THE INVENTION

Generally speaking the present invention contemplates the following formulations, the amounts being of the order of the quantities shown in parts by weight:

Formulation I	Formulation II	Formulation III	Formulation IV		
83% D-limonene	70% D-Limonene	73% D-limonene	65% D-Limonene		
17% Chloropicrin	18% Chloropicrin	14.5% Chloropicrin	13% Chloropicrin		
	14% Methyl	12.5% Diazinon	10% Methyl Isothiocyanate		
	Isothiocyanate	12% Diazinon			

BRIEF REVIEW OF THE PRIOR ART

Nematodes are a good example of undesirable soil components. Nematodes are microscopic eel worms and come in many varities. The dog hookworm is a nematode, i.e., it forms part of the animal parasitic 25 group. But, there are also those forming part of the plant parasitic group. These plant parasitic components feed on plant roots and poisons the plant. They also cause damage to the mammals, including humans who eat the plants. These undesirable soil components have 30 been controled by the injection into the soil of various formulations, one component suggested has been chloropicrin, but this component is very expensive and has not proven too effective, when carried out in practice. The use of chloropicrin has been suggested by Kirk et 35 al, "Encyclopedia of Chemical Technology" in its several editions in the article on Chloropicrin. Nevertheless, in practice, chloropicrin or Cl₃CNO₂ is not now used in the various commercially avilable formulations except as a warning agent for other fumigants.

Further inhibiting the use of chloropicrin is the tendency of chloropicrin to contaminate such items as beer and soda cans as described in the case of BURKE PEST CONTROL, INC. v. JOSEPH SCHLITZ BREWING COMPANY, 438 So. 2d 95 (Fla. App. 2 Dist. 1983), 45 wherein the brewing company discovered that after a fumigation treatment, from ten to sixty-six nanograms of chloropicrin remained on the can liners which contaminated the cans and made them useless.

Now it has been discovered that the undesirable effects of chloropicrin can be minimized and eliminated by using D-limonene (also called dl-limonene) as a solvent. D-limonene is a material of the terpene family. The terpene family has been most bountiful in providing the means to produce synthetic rubber and other valuable discoveries because of isoprene and the isoprene rule wherein carbon skeletons made of isoprene units are joined in a regular head-to-tail way, repeating the double bonds between molecules or other chemical particles. However, dl-limonene (the "dl" signifying 60 dextro-levo) is a solvent and as such usually does not enhance chemical reaction.

The present invention contemplates the use of D-limonene as a synergistic solvent in connection with the use of agricultural chemicals. Thus, it has now been 65 discovered that a formulation can be provided for the control of nematodes and similar undesirable soil components where the formulation makes use of D-limo-

DETAILED DESCRIPTION

As used herein, the terms hereinafter listed have the meanings shown next to the particular term:

D-limonene is 4-isopropenyl-1-methyl-1-cyclohexene. The structural formula is:

methyl isothiocyanate is CH₂SCN, being a member of the isocyanate family having the formula R—SCN, where "R" is a hydrocarbon radical

40 Diazinon is the trade name for phosphorothioic acid.

The structural formula is:

chloropicrin has the formula Cl₃CNO₂ and is otherwise known as trichloronitromethane

T is Telone, a Dow Chemical Co. product which is dichloropropene and has the formula:

$$\begin{array}{c|cccc} H_2 & H & H \\ & | & | & | \\ ClC - C = C \end{array}$$

C-17 is also known as Soilex is 17% Chloropicrin, 83% D-limonene

C-50 is 50 % chloropicrin, 50% D-limonene
Telone II is 92% dichloropropene

C-17-S is C-17 in a diazinon solution Vorlex is Telone II plus 20% methyl isothiocyanate

In carrying the invention into practice, various formulations were prepared having about 5 parts by weight and about 80 parts by weight of D-limonene as a solvent into which was added between about 10 parts

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by weight and about 90 parts by weight chloropicrin, namely, Cl₃CNO₂, additionally, in some of the formulations there was added about 80 parts by weight to about 20 parts by weight of methyl isothiocyanate. As a further formulation, several batches were prepared containing only D-limonene and methyl isothiocyanate, namely 10 parts by weight to about 50 parts by weight of the methyl isothiocyanate to about 50 parts by weight to about 90 parts by weight of the D-limonene solvent. Also, in some batches diazinon was added in 10 quantities of from zero to about 20 parts by weight.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given:

Formulations prepared by the applicant herein were 15 tested against formulations of the prior art at several locations in connection with various crops as shown:

(I) Location: Gainesville, Fla., University of Florida Institute of Food and Agricultural Sciences. Crop: Peanuts; Time August/October 1984 Formulations:

- (1) C-17 (hereinbefore described) "SOILEX"
- (2) Telone II 1-3-dichloropropane
- (3) Vorlex, 1-3-dichloropropane + 20% methyl isothiocyonate

The formulation used, namely 17% chloropicrin and 83% D-limonene had a specific gravity of 0.961 or approximately 8 Lbs. per gallon, a boiling point of 112° C., a freezing point of -81° C., a flash point greater than 130° F., vapor pressure at 20° C. of -17 mm Hg. 30 It is almost insoluble in water, soluble in alcohol, petroleum solvents, chlorinated solvents and carbon disulfide. In the presence of water, it becomes corrosive to steel, aluminum, magnesium alloys and vinyl plastics.

(II) Location: Boca Raton, Fla., Boca West Golf 35 Course.

Time: April, 1985 Formulations:

- (1) T, Telone (hereinbefore described)
- (2) C-17 (hereinbefore described)
- (3) C-17-S (hereinbefore described)
- (4) C-50 (hereinbefore described)
- (5) C-17-D is C-17 as hereinbefore described plus technical DIAZINON (92%)
- (III) Location: Tifton, Ga., Costal Plain Experiment Station, Donald Benson Farm, Tift County, Ga.

Crop: Peanuts; Time May/September 1984 Formulations:

- (1) T, Telone II
- (2) Vorlex
- (3) C-17, Soilex
- (4) Nemacur

Conclusion, in all the aforementioned tests the formulations described herein namely, D-limonene as a solvent with an effective amount of chloropicrin, and, also 20 by adding an effective amount of methyl-isothiocyanate, and/or with an effective amount of phosphorothioc acid were superior and usually vastly superior to the other formulations shown of the prior art. In the formulations tested, the D-lomonene solvent consist of 25 between about 5 to about 80 parts by weight and the chloropicrin may consist of between about 10 and about 90 parts by weight, the methyl-isothiocyanate component may be from about 20 to about 80 parts by weight, and may include between about zero to about 20 parts by weight of phosphorothioc acid. Another formulation which is effective consists of about 10 to about 50 parts by weight of methyl-isothiocyanate mixed into about 50 to about 90 parts by weight of D-limonene solvent. The combination of chloropicrin and methyl isothiocyanate is synergistic. With the further addition of diazinon, a double synergistic effect is obtained.

EVALUATION OF NEMATICIDES FOR MANAGING THE PEANUT ROOT-KNOT **NEMATODE ON PEANUT, 1984:** No. nematodes/250 cm³ soil Criconemella Meloidogyne Methods of appli-% % Value/ arenaria curvatum Yield Treatment and overall cation & rate per Oct 9 Aug 10 Oct 9 Aug 10 SMK Y lb/acre Damage 100 l. ft. row rate per acre (active) X 328bcdef 86bcdefg 191de $3,365a^{Z}$ 70 \$971 4b Telone II 15.0 gal 7 days preplant, 2-chisels, 10 inches apart; 65 ml 76bcdefg 276cdef 211de 69 944 10ab 3 3,332ab 14 days preplant, Telone II 15.0 gal 2-chisels 10 inches apart; 65 ml 15fg 138f 793ab 69 917 5ab 3 3,174abc Vorlex 12.0 gal 14 days preplant, 2-chisels, 8 inches apart ZZ ; 52 ml 103bcdef 110e 454abc 74 884 30ab 2,973abcd Telone II 12.0 gal + 14 days preplant, Temik 15 G 6.0 lb 2-chisels, 10 inches apart + at-peg, 14 inch band; 52 ml + 49 g150ef 5g 863 2b 864a 74 2,919abcd Vorlex 12.0 gal + 14 days preplant, 2-chisels, 8 inches Furadan 15 G 6.0 lb $apart^{ZZ} + at-peg 14$ inch band; 52 ml + 49 g196def 140abc 832 38ab 246cde 71 2 2,842abcd Telone II 6.0 gal 14 days preplant, 2-chisels, 10 inches apart; 26 ml 67bcdefg 453abc 850 4b 486bcde 73 2,842abcd Chloropicrin 6.0 gal 14 days preplant, 2-chisels, 10 inches apart; 26 ml 346abcde 78bcdefg 15ab 620abc 61 829 2,793abcd 2-chisels, Untreated Control 8 inches apart 367cde 132abcd 531a 64 17ab 776 3 2,766abcd 2-chisels, Untreated Control 10 inches apart 307cde 70bcdefg 512ab 69 784 19ab 3 2,717abcd Telone II 12.0 gal 14 days preplant,

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	EVALUATION OF NEMA	TICIDES FOR NEMATODE OF				NUT RO	OT-KNOT		
	2-chisels, 10 inches apart; 52 ml								
Telone II 12.0 gal +	14 days preplant,	2,690abcde	3	69	76 8	15ab	229cde	112bcde	378abcd
Furadan 15 G 6.0 lb	2-chisels, 10 inches apart + at-peg, 14 inch band; 52 ml + 49 g								
Chloropicrin 3.0 gal	14 days preplant, 2-chisels, 10 inches apart; 13 ml	2,624abcde	1	72	755	9ab	352cde	59cdefg	263cdef
Chloropicrin 9.0 gal	14 days preplant, 2-chisels, 10 inches apart; 39 ml	2,467bcde	5	55	682	43a	752ab	78bcdefg	254def
Telone II 9.0 gal	14 days preplant, 2-chisels, 10 inches apart; 39 ml	2,467bcde	8	65	688	26ab	337cde	193a	458abc
Busan 1020 30.0 gal	14 days preplant, 2-chisels, 8 inches apart; 130 ml	2,412cde	5	68	679	16ab	576abcd	40efg	193def
Busan 1020 36.0 gal	14 days preplant, 2-chisels, 8 inches apart; 156 ml	2,292de	5	71	662	37ab	465bcde	47defg	207def
Soilex C-17 15.0 gal	14 days preplant, 2-chisels, 10 inches apart; 65 ml	2,129de	6	52	578	10ab	422bcde	148ab	382abcd
Telone II 15.0 gal	at-plant, 2-chisels, 10 inches apart; 65 ml	1,851e	3	64	503	6ab	152e	50defg	502ab

Peanut (Arachis hypogaea 'Florunner')

Root-knot nematode; Meloidogyne arenaria

Ring nematode; Criconemella curvatum

D. W. Dickson and T. E. Hewlett Dept. Of Entomology & Nematology University of Florida Gainesville, Florida 32611

XRates calculated for row treatments were reduced from the overall (broadcast) dosage in proportion to the actual area tested. All dosages were calculated based on a 36 inch row

Sound mature kernels based on government grading system.

ZMeans with the same letter are not significantly different according to Duncan's new multiple range test (P = 0.05).

ZZRidged with diskhillers.

BOCA WEST TEST PLOTS							
BELONOLAIMUS ONLY							
PRE-TEST, 11 DAYS, & 34 DAYS AFTER INJECTION							

STING-BELO- 32 NOLAIMUS PRETEST 11 DAYS 24 ROOT NO RESPONSE @ 11 DAYS	CHECK 22	#2 TELONE 32 4 8 4 new root 1½" long	#3 C-17 + SAROLEX 24 20 24 NONE	#4 C-17 12 8 8 15 new	#5 C-17 + SAROLEX 48	#6 C-17 +	#7 TELONE 68	#8 C-50 24	#9 C-17 60	#10 TELONE 72
NEMATODE CI STING-BELO- 32 NOLAIMUS PRETEST 11 DAYS 24 34 DAYS 52 ROOT NO RESPONSE @ 11 DAYS	CHECK 2 2 4 52 NONE	#2 TELONE 32 4 8 4 new root 1½" long	C-17 + SAROLEX 24 20 24	C-17 12 8 8	C-17 + SAROLEX 48	C-17 + DIAZINON 52	TELONE 68	C-50 24	C-17	TELONE 72
NOLAIMUS PRETEST 11 DAYS 24 34 DAYS 52 ROOT NO RESPONSE @	24 NONE	4 8 4 new root 1½" long	20 24	8	8 4	12	4		60 4	
11 DAYS 24 34 DAYS 52 ROOT NO RESPONSE @ 11 DAYS	S2 NONE	8 4 new root 1½" long	24	8	4		4	12	4	17
ROOT NO RESPONSE @	NONE	4 new root 1½" long		_	4	24	30		•	16
RESPONSE @ 1 DAYS		1½" long	NONE	15 new	4	4 ™	28	8	36	
11 DAYS	POOR	_			4 new root	4 new	11 new	NONE	4 new	6 new
	POOR	GOOD S'		root 3" long	1" long	4" long	3" long		1" long	l½" long
VISUAL PO		G CLODE	POOR	POOR	POOR	GOOD 6'	GOOD 8'	POOR	POOR	GOOD 6'
RESPONSE @ 102 DAYS		of turf				of turf	of turf			of turf
	· · · · · · · · · · · · · · · · · ·			· · · · · · · · · · · · · · · · · · ·		SAMPLE N	UMBER			
			#11			#14		į	#17	
			C-17 +	#12	#13	C-17 +	#15	#16	C-17 +	#18
	•	NEMATODE	DIAZINO	N CHECK	C-50	DIAZINON	I C-50	C-17	SAROLE	K CHECI
	•	STING-BELO- NOLAIMUS PRETEST	32	36	36	36`	12	16	80	48
		11 DAYS	0	48	12	8	16	16	56	28
		34 DAYS	16	4	12	Ö	0		14	84
		ROOT	NONE	NONE	NONE	NONE	6 new	_	NONE	NONE
		RESPONSE @					3" long	2" long		
	•	11 days VISUAL RESPONSE @ 102 days	GOOD 8'	POOR	GOOD 5'	GOOD 20'	POOR	POOR	POOR	POOR
		· · · · · · · · · · · · · · · · · · ·	NEM	ATODE T	hree Plot Av	erage Below				
		CF	HECK TI	ELONE	C-17 + S	C-17 C	·17 + D	C-50		

	NEWATODE THEE FIOLAVEIAGE DELOW								
	CHECK	TELONE	C-17 + S	C-17	C-17 + D	C-50			
PRETEST 11 DAYS		57 8 86% ↓	51 28 45%↓	29 9 69%↓	40 7 83%↓	24 13 46%↓			

-continued

BOCA WEST TEST PLOTS BELONOLAIMUS ONLY PRE-TEST, 11 DAYS, & 34 DAYS AFTER INJECTION

24 53% 17 41% 1 13 68% ↓ 71% 34 DAYS 21% † 25 56% ↓

When the number of nematodes are estimated the following symbols are used:

VL—very light infestation; L—light infestation;

MM—moderate infestation;

H—heavy infestation;

VH—very heavy infestation.

Experiment No. and Title: P5-84. Comparison of Soilex and Telone II applied to peanut 8 days preplant.

Work Unit/Project No.: 7702-20270-001

Address: Coastal Plain Experiment Station, Tifton, GA 15 Work Unit/Project No.: 7702-20270-001 31793

Investigator(s): Norman A. Minton and A. S. Csinos Experiment Location: Donald Benson Farm, Tift, County

Type Experiment: Field

Nematode species: Meloidogyne arenaria, Criconemella ornata

Other Organisms:

Plant species and varieties: Arachis hypogaea, Florunner

Experimental design: Strip

Plot size and No. reps.: 2 rows, 25 ft long, 4 replications.

Soil type: Ocilla loamy soil

Soil moisture: 10.7%, May 2 when chemicals applied Soil temperature: Maximum, 84 F., minimum, 73 F. at

4" depth when chemicals applied.

Planting dates: May 10 Treatment dates: May 2 Harvest dates: September 24

Weather conditions: Adequate rainfall for good yields

Unusual circumstances:

Progress: See Table P5A-84.

Experiment No. and Title: P6-84. Fumigant nematicides: Methods of application to peanut 8 days preplant.

Address: Coastal Plain Experiment Station, Tifton, GA 31793

Investigator(s): Norman A. Minton and A. S. Csinos Experiment Location: Donald Benson Farm, Tift

County

Type Experiment: Field

Nematode species: Meloidogyne arenaria, Criconemella ornata

Other Organisms:

25 Plant species and varieties: Arachis hypogaea, Florunner Experimental design: Strip

Plot size and No. reps.: 2 rows, 25 ft long, 4 replications

Soil type: Ocilla loamy soil

Soil moisture: 10.7% May 2 when fumigant nematicides applied.

Soil temperature: Maximum, 84 F.; minimum, 73 F. at 4" depth when the chemicals applied.

Planting dates: May 10

Treatment dates: Fumigants, May 2; Nemacur, May 10

35 Harvest dates: September 24

Weather conditions: Adequate rainfall for good yields

Number nematodes/

TABLE P5A-84

		Yield (lb/A)			White mold hits ⁵	Stand (5/21) ⁶	Vigor rating (6/22) ⁷	Number nematodes/ 150 cm ³ soil, 9/14/84	
Treatment and rate (lb ai/A)	Method of ² application		% SMK ³	Root- knot index ⁴				Crico- nemella ornata	Meloido- gyne arenaria
Telone II 55.8 Soilex 117.6 Control	A A	4857 ab 5162 a 4552 b	80.0 79.7 78.7	3.1 a 3.9 a 5.9 a	3.3 a 3.3 a 4.8 a	12.0 a 12.0 a 13.3 a	3.5 b 4.3 ab 4.5 a	2425 a 1545 a 2052 a	530.0 a 422.5 a 1475.0 a

¹Data within same column followed by the same letter are not significantly different (P = 0.05) according to Duncan's multiple-

range test.

²Applied in moldboard plow furrow 10" deep on 8" centers 8 days before planting.

⁵White mold hits = number of hits per 50 ft row. One or more plants infected per ft of row in one hit.

⁶Stand = number of plants emerged per m of row.

Unusual circumstances: Progress: See Table P6-84.

TABLE P6A-84

Effects of three fumigant nematicides applied with moldboard plow and single chisel on peanut production, 1984.1

			% SMK ³					150 cm ³ soil, 9/14/84		
Treatment and rate (lb ai/A)	Method of ² application	Yield (lb/A)		Root- knot index ⁴	White mold hits ⁵	Stand (5/21) ⁶	Vigor rating (6/22) ⁷	Crico- nemella ornata	Meloido- gyne arenaria	
Telone II 37.2	A	4640 ab	76.7	4.3 bc	3.0 ъ	12.4 a	2.5 bc	3097 a	932.5 b	
Vorlex 38.4	Α	2975 с	74.0	9.5 a	18.0 a	13.3 a	2.3 c	1652 bc	2297.5 a	
Telone II 37.2	В	4852 ab	79.7	2.9 cd	3.3 b	11.6 a	3.5 a	2782 ab	435.0 ъ	
Vorlex 38.4	В	4360 b	76.0	3.4 cd	3.8 ъ	11.9 a	3.0 a-c	1702 a-c	522.5 Ъ	

³% sound mature kernel (SMK) determined from composit sample from four replications. ⁴Root-knot index based on rating of 0–10: 0 = no galling, 10 = 100% of roots and pods galled.

⁷Vigor rating based on scale of 1-5: 1 = poor growth, 5 = excellent growth.

TABLE P6A-84-continued

Effects of three fumigant nematicides applied with moldboard plow and single chisel on peanut production, 1984.1

> Number nematodes/ 150 cm³ soil,

								9/14/84		
Treatment and rate (lb ai/A)	Method of ² application	Yield (lb/A)	% SMK ³	Root- knot index ⁴	White mold hits ⁵	Stand (5/21) ⁶	Vigor rating (6/22) ⁷	Crico- nemella ornata	Meloido- gyne arenaria	
Soilex CP 39.2	В	4476 b	78.3	4.1 bc	3.0 ь	11.3 a	3.0 a-c	2597 ab	700.0 b	
Nemacur 15 G 2.5	C	5064 a	78.7	1.4 d	3.3 b	11.6 a	3.3 ab	667 c	470.0 b	
Control		4325 b	77.0	6.2 b	3.5 b	12.9 a	3.3 ab	1350 bc	1135.0 ь	

¹Data within same column followed by the same letter are not significantly different (P = 0.05) according to Duncan's multiple-range test.

What is claimed is:

1. A nematocidal agricultural formulation for the control of nematodes consisting essentially of a D-limonene solvent and between 15% and 20% of chloropicrin, the percentage being by weight.

2. A method of controlling nematode infestation com- 25

prising applying to said nematodes or the habitate thereof a composition consisting essentially of a D-limonene solvent and between 15% and 20% by weight of chloropicrin.

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²Method of application: A = applied in moldboard plow furrow 10" deep spaced 8" apart 8 days before planting, B = injected 10" deep in row with single chisel 8 days before planting, C = applied in 12" band over row, rototilled 2" deep at plant.

³% sound mature kernel (SMK) determined from composit sample from four replications.

⁴Root-knot index based on rating of 0-10: 0 = no galling, 10 = 100% of roots and pods galled.

⁵White mold hits = number of hits per 50 ft row. One or more plants infected per ft of row is one hit.

⁶Stand = number of plants emerged per m of row.

⁷Vigor rating based on scale of 1-5: 1 = poor growth, 5 = excellent growth.